

# Modeling Oil and Petroleum Evaporation

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## Abstract

Evaporation is an important component in oil spill models. Various approaches for oil evaporation prediction are summarized. Models can be divided into those models that use the basis of air-boundary-regulation or those that use liquid diffusion-regulated evaporation physics. Studies show that oil is not air boundary-layer regulated such as it is for water evaporation, which implies that a simplistic evaporation equation suffices to accurately describe the process. The following processes do not require consideration: wind velocity, turbulence level, area and scale size. The factors important to evaporation are time and temperature. Oil evaporation does show a thickness effect, although not as pronounced as that for air-boundary-layer regulated models. A thickness adjustment calculation is presented for diffusion-regulated models. This new model is applicable to thicknesses greater than about 1.5 mm. In the case of thin slicks, this adjustment is not relevant as oils typically spread to less than that in a short time.

The use of air-boundary-models results in three types of errors: air-boundary-layer models cannot accurately deal with long term evaporation; second, the wind factor results in unrealistic values and finally, they have not been adjusted for the different curvature for diesel-like evaporation. Further, these semi-empirical equations require inputs such as area, etc., that are unknown at the time of the spills. There has been some effort on the part of modellers to adjust air-boundary-layer models to be more realistic on the long-term, but these may be artificial and result in other errors such as under-estimation for long-term prediction. A comparison of models shows that on a very short term, such as a few hours, most models yield similar results. However, as time increases past a few days, the errors with air-boundary-layer regulated models are unacceptable. Examples are given where errors are as large as 100% over a few days.

## Keywords

*Oil Spill Evaporation; Hydrocarbon Evaporation; Evaporation Modeling*

## Introduction

Evaporation is an important process for most oil spills. Almost all oil spill models include evaporation as a process and output of the model. Evaporation plays a

prime role in the fate of most oils. In a few days, typical crude oils can lose up to 45% of their volume (Fingas 2011). The Deepwater Horizon oil lost up to 55% in a short time when released under water at high pressure. Many crude oils must undergo evaporation before the formation of water-in-oil emulsions. Light oils will change very dramatically from fluid to viscous; while heavy oils will become solid-like. Many oils after long evaporative exposure, form tar balls or heavy tar mats. Despite the importance of the process, only some work has been conducted on the basic physics and chemistry of oil spill evaporation (Fingas 1995). The difficulty in studying oil evaporation is that oil is a mixture of hundreds of compounds and oil composition varies from source to source and even over time. Much of the work described in the previous literature focused on calibrating equations developed for water evaporation (Fingas 1995).

The mechanisms that regulate evaporation are important (Brutsaert 1995; Jones 1992). Evaporation of a liquid can be considered as the movement of molecules from the surface into the vapour phase above it. The immediate layer of air above the evaporation surface is known as the air boundary layer<sup>5</sup> which is the intermediate interface between the air and the liquid and might be viewed as very thin e.g. as less than 1 mm. The characteristics of this air boundary layer can influence evaporation. In the case of water, the boundary layer regulates the evaporation rate. Air can hold a variable amount of water, depending on temperature, as expressed by the relative humidity. Under conditions where the air boundary layer doesn't move (no wind) or has low turbulence, the air immediately above the water quickly becomes saturated and evaporation slows. The actual evaporation of water proceeds at a small fraction of the possible evaporation rate because of the saturation of the boundary layer. The air-boundary-layer physics is then said to regulate the evaporation of water. This regulation manifests the increase of evaporation with wind or turbulence. When

turbulence is weak, evaporation can slow down by orders-of-magnitude. The molecular diffusion of water molecules through air is at least  $10^3$  times slower than turbulent diffusion (Monteith and Unsworth 2008).

Some liquids are not air-boundary-layer regulated primarily because they evaporate too slowly to make the vapours saturate the air boundary layer above them (Fingas 2011). Many mixtures are regulated by the diffusion of molecules inside the liquid to the surface of the liquid. Such a mechanism is true for many slowly-evaporating mixtures of compounds such as oils and fuels. Some of the outcomes of this mechanism may seem counterintuitive to some people such as that increasing area may not necessarily increase evaporation rate. More importantly, increasing wind speed does not increase evaporation.

Scientific work on water evaporation dates back decades and thus the basis for early oil evaporation work has been established (Fingas 2011). There are several fundamental differences between the evaporation of a pure liquid such as water and that of a multi-component system such as crude oil. The evaporation rate for a single liquid such as water is a constant with respect to time. Evaporative loss, either by weight or volume, is not linear with time for crude oils, and other multi-component fuel mixtures (Fingas 1997).

### Review of Historical Developments

For air-boundary-layer regulated liquids, one can write the mass transfer rate in semi-empirical form as (Fingas 2011):

$$E = K C T_u S \quad (1)$$

where  $E$  is the evaporation rate in mass per unit area,  $K$  is the mass transfer rate of the evaporating liquid, sometimes denoted as  $k_g$  (gas phase mass transfer coefficient, which may incorporate some of other parameters noted here),  $C$  is the concentration (mass) of the evaporating fluid as a mass per volume,  $T_u$  is a factor characterizing the relative intensity of turbulence, and  $S$  is a factor related to the saturation of the boundary layer above the evaporating liquid. The saturation parameter,  $S$ , represents the effects of local advection on saturation dynamics. If the air has already been saturated with the compound in question, the evaporation rate approaches zero. This also relates to the scale length of an evaporating pool. If one views a large pool over which a wind is blowing, there is a

high probability that the air is saturated downwind and the evaporation rate per unit area is lower than that for a smaller pool. It is noted that there are many equivalent ways to express this fundamental evaporation equation. These will be seen in the equations below.

Sutton proposed the following equation based on empirical work (Brutsaert 1982):

$$E = K C_s U^{7/9} d^{-1/9} Sc^{-r} \quad (2)$$

where  $C_s$  is the concentration of the evaporating fluid (mass/volume),  $U$  is the wind speed,  $d$  is the area of the pool,  $Sc$  is the Schmidt number and  $r$  is the empirical exponent assigned values from 0 to 2/3. Other parameters are defined as above. The terms in this equation are analogous to the very generic equation, (1), proposed above. The turbulence is expressed by a combination of the wind speed,  $U$ , and the Schmidt number,  $Sc$  that is the ratio of kinematic viscosity of air ( $\nu$ ) to the molecular diffusivity ( $D$ ) of the diffusing gas in air, i.e., a dimensionless expression of the molecular diffusivity of the evaporating substance in air.<sup>7</sup> The coefficient of the wind power typifies the turbulence level. The value of 0.78 (7/9) as chosen by Sutton, represents a turbulent wind whereas a coefficient of 0.5 would represent a wind flow that is more laminar. The scale length represented by  $d$  has been given an empirical exponent of -1/9. This represents for water, a weak dependence on size. The exponent of the Schmidt number,  $r$ , represents the effect of the diffusivity of the particular chemical, and historically was assigned values between 0 and 2/3 (Sutton 1934).

Blokkeer was the first to develop oil evaporation equations for oil evaporation at sea, with his partially theoretical starting basis (Blokkeer, 1964). Oil was presumed to be a one-component liquid. The distillation data and the average boiling points of successive fractions were used as the starting point to predict an overall vapour pressure. The average vapour pressure of these fractions was then calculated from the Clausius-Clapeyron equation to yield:

$$\log \frac{p_s}{p} = \frac{qM}{4.57} \left( \frac{1}{T} - \frac{1}{T_s} \right) \quad (3)$$

where  $p$  is the vapour pressure at the absolute temperature,  $T$ ;  $p_s$  is the vapour pressure at the boiling point,  $T_s$  (for  $p_s$ , 760 mm Hg was used);  $q$  is the heat of evaporation in cal/g and  $M$  is the molecular weight.

The term  $qM/(4.57 T_s)$  was taken to be nearly constant

for hydrocarbons ( $\approx 5.0 \pm 0.2$ ) and thus the expression was simplified to

$$\log p_s/p = 5.0 [(T_s - T)/T] \quad (4)$$

From the empirical data and equation (4), the weathering curve was calculated, assuming that Raoult's law is valid for this situation giving  $q_M$  as a function of the percentage evaporated. Pasquill's equation was applied stepwise, and the total evaporation time was obtained by summation:

$$t = \frac{\Delta h D^\beta}{K_{ev} U^\alpha} \sum \frac{1}{PM} \quad (5)$$

where  $t$  is the total evaporation time in hours,  $\Delta h$  is the decrease in layer thickness in m,  $D$  is the diameter of the oil spill,  $\beta$  is a meteorological constant (assigned a value of 0.11),  $K_{ev}$  is a constant for atmospheric stability (taken to be  $1.2 \times 10^{-8}$ ),  $\alpha$  is a meteorological constant (assigned a value of 0.78),  $P$  is the vapour pressure at the absolute temperature,  $T$ ; and  $M$  is the molecular weight of the component or oil mass. Tests of this equation by experimental evaporation using a small wind tunnel did not yield good correspondence to test data.

Mackay and Matsugu (1973) approached evaporation by using the classical water evaporation and experimental work. The water evaporation equation was corrected to hydrocarbons using the evaporation rate of cumene. Data on the evaporation of water and cumene have been used to correlate the gas phase mass transfer coefficient as a function of wind-speed and pool size by the equation,

$$K_m = 0.0292 U^{0.78} X^{-0.11} Sc^{-0.67} \quad (6)$$

Where  $K_m$  is the mass transfer coefficient in units of mass per unit time and  $X$  is the pool diameter or the scale size of evaporating area. Note that the exponent of the wind speed,  $U$ , is 0.78 equal to the classical water evaporation-derived coefficient. Mackay and Matsugu noted that for hydrocarbon mixtures the evaporation process is more complex, dependent on the liquid diffusion resistance being present.<sup>9</sup> Experimental data on gasoline evaporation were compared with computed rates which showed some deviations from the experimental values and suggested the presence of a liquid-phase mass-transfer resistance. The same group showed that the evaporative loss of a mass of oil spilled can be estimated using a mass transfer coefficient,  $K_m$ , as shown above (Goodwin et al. 1976). This approach was investigated with some laboratory data and tested against some known mass transfer conditions on the

sea Butler (1976) developed a model to examine evaporation of specific hydrocarbon components. The weathering rate was taken as proportional to the equilibrium vapour pressure,  $P$ , of the compound and to the fraction remaining:

$$dx/dt = -kP(x/x_o) \quad (7)$$

where  $x$  is the amount of a particular component of a crude oil at time,  $t$ ,  $x_o$  is the amount of that same component present at the beginning of weathering ( $t = 0$ ),  $k$  is an empirical rate coefficient and  $P$  is the vapour pressure of the chosen oil component.

Butler assumed that petroleum is a complicated mixture of compounds, therefore  $P$  is not equal to the vapour pressure of the pure compound, but neither would there be large variation in the activity coefficient as the weathering process occurs (Butler 1976). For this reason, the activity coefficients were subsumed in the empirical rate coefficient  $k$ .  $P$  and  $k$  were taken as independent of the amount,  $x$ , for a fairly wide range of oils. The equation was then directly integrated to give the fraction of the original compound remaining after weathering as:

$$x/x_o = \exp(-ktP/x_o) \quad (8)$$

The vapour pressure of individual components was fit using a regression line to yield a predictor equation for vapour pressure:

$$P = \exp(10.94 - 1.06 N) \quad (9)$$

where  $P$  is the vapour pressure in Torr and  $N$  is the carbon number of the compound in question. This combined with equation (8) and yielded the following expression:

$$x/x_o = \exp [-(kt/x_o)\exp(10.94 - 1.06 N)] \quad (10)$$

Where  $x/x_o$  is the fraction of the component left after weathering,  $k$  is an empirical constant,  $x_o$  is the original quantity of the component and  $N$  is the carbon number of the component in question. Equation (10) predicts that the fraction weathered is a function of the carbon number and decreases at a rate that is faster than predicted from simple exponential decay.<sup>12</sup> If the initial distribution of compounds is essentially uniform ( $x_o$  independent of  $N$ ), then the above equation predicts that the carbon number where a constant fraction (e.g. half) of the initial amount has been lost ( $x = 0.5 x_o$ ) is a logarithmic function of the time of weathering:

$$N_{1/2} = 10.66 + 2.17 \log (kt/x_o) \quad (11)$$

where  $N_{1/2}$  is half of the volume fraction of the oil. The equation was tested using evaporation data from some patches of oil on shoreline, whose age was known. The equation was capable of predicting the age of the samples relatively well. It was suggested that the equation was applicable to open water spills; however, this was never subsequently applied in models.

Yang and Wang (1977) developed an equation using the Mackay and Matsugu molecular diffusion process.<sup>2</sup> The vapour phase mass transfer process was expressed as:

$$D_{ie} = \frac{k_m (p_i - p_{i\infty})}{[RT_s]} \quad (12)$$

where  $D_{ie}$  is the vapour phase mass transfer rate,  $k_m$  is a coefficient that lumps all the unknown factors affecting the value of  $D_{ie}$ ,  $p_i$  is the hydrocarbon vapour pressure of fraction,  $I$ , at the interface,  $p_{i\infty}$  is the hydrocarbon vapour pressure of fraction,  $I$ , at infinite altitude of the atmosphere,  $R$  is the universal gas constant and  $T_s$  is the absolute temperature of the oil slick. The following functional relationship was proposed (Yang and Wang 1977):

$$k_m = \alpha A^a e^{qU} \quad (13)$$

where  $A$  is the slick area,  $U$  is the over-water wind speed, and  $a$ ,  $q$  and  $\gamma$  are empirical coefficients. This relationship was based on the results of previous studies, including, for instance, those of MacKay and Matsugu who suggested the value of  $\gamma$  to be in the range from -0.025 to -0.055.<sup>9</sup> Further experiments were performed by Yang and Wang to determine the values of ' $a$ ' and ' $q$ '. Experiments showed that a film formed on evaporating oils and this film severely retarded evaporation. Before the surface film has developed ( $Q_t/Q_o < 1.0078$ ):

$$K_{mb} = 69 A^{-0.0055} e^{0.42U} \quad (14)$$

where  $K_{mb}$  is the coefficient that groups all factors affecting evaporation before the surface film has formed and  $A$  is the area. After the surface film has developed ( $Q_t/Q_o > 1.0078$ )

$$K_{ma} = 1/5 K_{mb} \quad (15)$$

where  $Q_o$  is initial oil density,  $Q_t$  is weathered oil density at time  $t$ , and  $K_{ma}$  is the coefficient that groups all factors affecting evaporation after the surface film has formed.<sup>12</sup> The evaporation rate was found to be reduced fivefold after the formation of the surface film.

Drivas (1982) compared the Mackay and Matsugu equation with data found in the literature and noted

that the equations yielded predictions that were close to the experimental data. Rheijnhart and Rose (1982) developed a simple predictor model for the evaporation of oil at sea and proposed the following simple relationship:

$$Q_{ei} = \alpha C_o \quad (16)$$

where  $Q_{ei}$  is the evaporation rate of the component of interest,  $\alpha$  is a constant incorporating wind velocity and other factors (taken as  $0.0009 \text{ m s}^{-1}$ ) and  $C_o$  is the equilibrium concentration of the vapour at the oil surface. Several pan experiments were run to simulate evaporation at sea and the data used to test the equation. No method was given to calculate the essential value,  $C_o$ .

Brighton (1985,1990) proposed that the standard formulation used by many workers required refining. His starting point for water evaporation was similar to that proposed by Sutton:

$$E = K_m C_s U^{7/9} d^{1/9} Sc^r \quad (17)$$

where  $E$  is the mean evaporation rate per unit area,  $K_m$  is an empirically-determined constant, presumably related to the foregoing mass transfer constant,  $C_s$  is the concentration of the evaporation fluid (mass/volume),  $d$  is the area of the pool and  $r$  is an empirical exponent assigned values from 0 to 2/3. Brighton suggested that this equation should conform to the basic dimensionless form involving the parameters  $U$  and  $Z_o$  (wind speed and roughness length, respectively) which define the boundary layer conditions. The key factor in Brighton's analysis was to use a linear eddy-diffusivity profile. This feature implied that concentration profiles become logarithmic near the surface, which is suspected to be more realistic compared to the more finite values previously used. Using a power profile to provide an estimation of the turbulence, Brighton was able to substitute the following identities into the classical relationship:

$$U = \frac{u^*}{k} n \quad (18)$$

$$n = \left( \ln \frac{z_1}{z_0} \right) \quad (19)$$

Where:  $u^*$  is the friction velocity,  $z_1$  is the reference height above the surface,  $z_0$  is the roughness length and  $n$  is the power law dimensionless term. The evaporation equation now became:

$$U \left( \frac{z}{z_1} \right) \frac{\delta X}{\delta x} = \frac{\delta}{\delta z} \left( \frac{k u^* z}{\sigma} \right) \left( \frac{\delta X}{\delta z} \right) \quad (20)$$

where  $z$  is the height above the surface,  $X$  is the concentration of the evaporating compounds,  $x$  is the dimension of the evaporating pool,  $k$  given by  $K/u^*z$ , is the von Karman constant and  $\sigma$  is the turbulent Schmidt number (taken as 0.85). Brighton subsequently compared his model with experimental evaporation data in the field and in the laboratory, including laboratory oil evaporation data (Brighton 1985, 1990). The model only correlated well with laboratory water evaporation data and the reason given was other data sets were 'noisy'.

Tkalin (1986) proposed a series of equations to predict evaporation at sea:

$$E_i = \frac{K_a M_i P_{oi} x_i}{RT} \quad (21)$$

where  $E_i$  is the evaporation rate of component  $i$  (or the sum of all components) ( $\text{kg/m}^2\text{s}$ ),  $K_a$  is the mass transfer coefficient ( $\text{m/s}$ ),  $M_i$  is the molecular weight,  $P_{oi}$  is the vapour pressure of the component  $i$ , and  $x_i$  is the amount of component  $i$  at time,  $t$ . Using empirical data, relationships were developed for some of the factors in the equation:

$$P_{oi} = 10^3 e^A \quad (22)$$

$$\text{where } A = -(4.4 + \log T_b)[1.803\{T_b/T - 1\} - 0.803 \ln(T_b/T)] \quad (23)$$

and where  $T_b$  is the boiling point of the hydrocarbon, given as

$$K_a = 1.25U^{10^{-3}} \quad (24)$$

The equations were verified using empirical data from the literature.

A frequently used work in older spill modelling is that of Stiver and Mackay (1984) based on some of the earlier work of Mackay and Matsugu (1973). The formulation was initiated with assumptions on the evaporation of a liquid. If a liquid is spilled, the rate of evaporation is given as:

$$N = KAP/(RT) \quad (25)$$

where  $N$  is the evaporative molar flux ( $\text{mol/s}$ ),  $K$  is the mass transfer coefficient under the prevailing wind ( $\text{ms}^{-1}$ ) and  $A$  is the area ( $\text{m}^2$ ),  $P$  is the vapour pressure of the bulk liquid. This equation was arranged to give:

$$dF_v/dt = KAP_v/(V_o RT) \quad (26)$$

where  $F_v$  is the volume fraction evaporated,  $v$  is the liquid's molar volume ( $\text{m}^3/\text{mol}$ ) and  $V_o$  is the initial volume of spilled liquid ( $\text{m}^3$ ). By rearranging:

$$dF_v = [P_v/(RT)](KA dt/V_o) \quad (27)$$

$$\text{or } dF_v = H d\theta \quad (28)$$

where  $H$  is Henry's law constant and  $\theta$  is the evaporative exposure (defined below).

The right-hand side of the second last equation has been separated into two dimensionless groups (Stiver and MacKay 1984). The group,  $KA dt/V_o$ , represents the time-rate of what has been termed as the "evaporative exposure" and was denoted as  $d\theta$ . The evaporative exposure is a function of time, the spill area and volume (or thickness), and the mass transfer coefficient (which is dependent on the wind speed). The evaporative exposure can be viewed as the ratio of exposed vapour volume to the initial liquid volume.<sup>18</sup>

The group  $P_v/(RT)$  or  $H$  is a dimensionless Henry's law constant or ratio of the equilibrium concentration of the substance in the vapour phase  $[P/(RT)]$  to that in the liquid ( $l/v$ ).  $H$  is a function of temperature. The product  $\theta H$  is thus the ratio of the amount which has evaporated (oil concentration in vapour times vapour volume) to the amount originally present. For a pure liquid,  $H$  is independent of  $F_v$  and equation 26 was integrated directly to give:

$$F_v = H \theta \quad (29)$$

If  $K$ ,  $A$ , and temperature are constant, the evaporation rate is constant and evaporation is complete ( $F_v$  is unity) when  $\theta$  achieves a value of  $1/H$ .

If the liquid is a mixture,  $H$  depends on  $F_v$  and the basic equation can only be integrated if  $H$  is expressed as a function of  $F_v$ ; i.e., the principal variable of vapour pressure is expressed as a function of composition. The evaporation rate slows as evaporation proceeds in such cases. Equation (27) was replaced with a new equation developed using laboratory empirical data:

$$F_v = (T/K_1) \ln(1 + K_1 \theta/T) \exp(K_2 - K_3/T) \quad (30)$$

where  $F_v$  is the volume fraction evaporated and  $K_{1,2,3}$  are empirical constants.<sup>18</sup> A value for  $K_1$  was obtained from the slope of the  $F_v$  vs.  $\log \theta$  curve from pan or bubble evaporation experiments. For  $\theta$  greater than  $10^4$ ,  $K_1$  was found to be approximately  $2.3T$  divided by the slope. The expression  $\exp(K_2 - K_3/T)$  was then calculated, and  $K_2$  and  $K_3$  were determined individually from evaporation curves at two different temperatures.

Hamoda and co-workers (1989) performed theoretical and experimental work on evaporation. An equation

was developed to express the effects of API<sup>o</sup> (American Petroleum Institute gravity—a unit of density) of the crude oil, temperature, and salinity on the mass transfer coefficient K:

$$K = 1.68 \times 10^{-5} (\text{API}^o)^{1.253} (T)^{1.80} e^{0.1441} \quad (31)$$

where K is the mass transfer coefficient, cm h<sup>-1</sup>, API<sup>o</sup> is the density in API units, unitless, and e is the water salinity in degrees salinity or parts-per-thousand. The exponents of the equation were determined by multiple linear regression on experimental data.

Quinn and co-workers (1990) weathered oils in a controlled environment and correlated the data with equations developed starting with Fick's diffusion law and the Clausius-Clapeyron equation. Crude oil was divided into a series of pseudo fractions by boiling point. Each fraction was taken to be equivalent to an n-paraffin. The n-paraffin distributions of a number of naturally weathered crude oils were determined by capillary gas-liquid chromatography. The actual measured evaporation was compared with those generated by computer simulation of weathering.

Bobra (1992) conducted laboratory studies on the evaporation of crude oils. The evaporation curves for several crude oils and petroleum products were measured under several different environmental conditions. These data were compared to the equation developed by Stiver and Mackay (1984). The equation used was:

$$F_v = \ln[1 + B(T_G/T) \theta \exp(A - B T_o/T)] \{T/BT_G\} \quad (32)$$

where F<sub>v</sub> is the fraction evaporated, T<sub>G</sub> is the gradient of the modified distillation curve, A and B are dimensionless constants, T<sub>o</sub> is initial boiling point of the oil and θ is the evaporative exposure as previously defined. The constants for the above equation and the results from several comparison runs were carried out.<sup>21</sup> The agreement between the experimental data and the equation results were poor in most cases. This comparison showed that the Stiver and Mackay equation predicts the evaporation of most oils relatively well until time approaches 8 hours, after that it over-predicted the evaporation. The 'overshoot' could be as much as 10% evaporative loss at the 24-hour mark. This is especially true for very light oils. The Stiver and Mackay equation was also found to under-predict or over-predict the evaporation of oils in the initial phases. Bobra also noted that most oil evaporation follows a logarithmic curve with time and that a simple approach to this was much more accurate than using equation (30).

In summary, it is difficult to develop a theoretical approach to oil evaporation for several reasons. First, oil consists of many components and thus there is no constant boiling point, vapor pressure or other essential properties used in typical evaporation models. Further, oil evaporation proceeds by diffusion regulation but not by air-boundary-layer regulation. Water evaporation models cannot be accurately modified to oil evaporation for these reasons.

### Development of Diffusion-Regulated Models

The review of the predictive and theoretical work in section 2 above reveals those air-boundary-layer concepts that are limited and cannot accurately explain long-term evaporation. Fingas conducted a series of experiments over several years to examine the concepts (Fingas 1998, 2011).

### Wind Experiments

A simple experiment to determine whether or not oil evaporation is air-boundary-layer regulated is to measure if the evaporation rate increases with wind as predicted by equations (2) and (6) above. Experiments on the evaporation of oil with and without winds were conducted with ASMB (Alberta Sweet Mixed Blend), gasoline, and with water. Water formed a baseline data set since this is the substance being compared.<sup>4</sup> Regressions on the data were performed and the equation parameters calculated. Curve coefficients are the constants from the best fit equation [Evap = a ln(t)], t=time in minutes, for logarithmic equations or Evap=a√t, for the square root equations. Oils such as diesel fuel with fewer sub-components evaporating at one time, have a tendency to fit square root curves (Fingas 2011, Li et al. 2004). While data were calculated separately for percentage of weight lost and absolute weight, the latter are usually used because it is more convenient. The plots of wind speed versus the evaporation rate (as a percentage of weight lost) for each oil type are shown in Figures 1 to Figure 3. These figures show that the evaporation rates for oils and even the light product, gasoline, are not increased with increasing wind speed. The evaporation rate after the 0-wind value is nearly identical for all oils, resulting from the stirring effect on the oil which increases the diffusion rate to the surface. Stirring will increase the diffusion and therefore the evaporation rate. The oil evaporation data can be compared to the evaporation of water, as illustrated in Figure 4. These data show the classical relationship of the water evaporation rate correlated with the wind speed (evaporation varies as



$U^{0.78}$ , where  $U$  is wind speed). This comparison shows that the oils studied here are not air boundary-layer regulated.

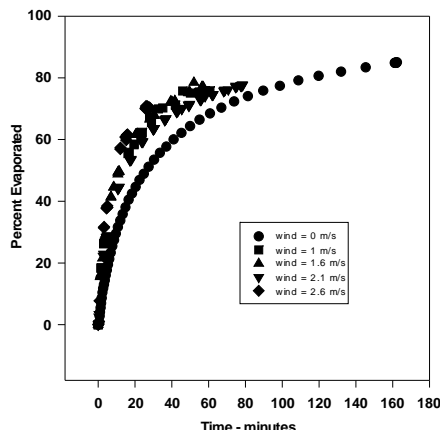


FIG. 1 EVAPORATION OF GASOLINE WITH VARYING WIND VELOCITIES. THIS FIGURE ALSO SHOWS THAT THERE IS LITTLE VARIATION WITH WIND VELOCITY EXCEPT IN GOING FROM THE 0-WIND-LEVEL UP TO THE OTHERS. THIS IS DUE TO THE STIRRING EFFECT OF WIND AND NOT AIR-BOUNDARY LAYER REGULATION.

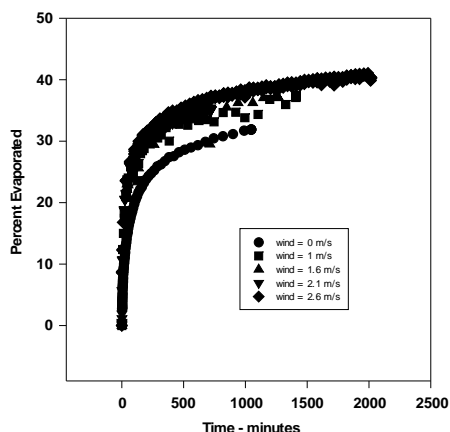


FIG. 2 VAPORATION OF ALBERTA LIGHT CRUDE OIL WITH VARYING WIND VELOCITIES. THIS FIGURE SHOWS THAT THERE IS LITTLE VARIATION WITH WIND VELOCITY EXCEPT IN GOING FROM THE 0-WIND-LEVEL UP TO THE OTHERS. THIS IS DUE TO THE STIRRING EFFECT OF WIND AND NOT AIR-BOUNDARY LAYER REGULATION.

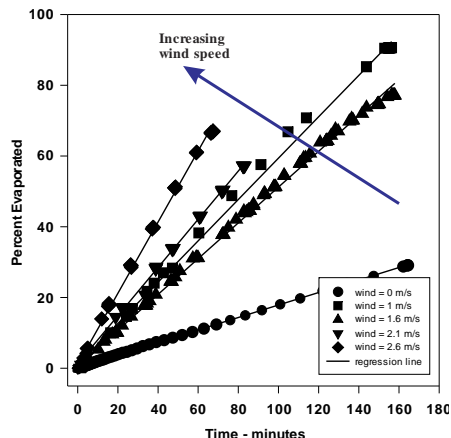


FIG. 3 EVAPORATION OF WATER WITH VARYING WIND VELOCITIES. THIS FIGURE SHOWS DRAMATIC DIFFERENCES

IN THE EVAPORATION RATE OF WATER WITH WIND VELOCITY. THIS IS TYPICAL OF AIR-BOUNDARY-LAYER REGULATION. COMPARE FIGURE 3 WITH OIL EVAPORATION IN FIGURES 1 AND 2 WHICH DO NOT SHOW THIS TREND OF VARIANCE WITH WIND VELOCITY.

Figure 4 shows the rates of evaporation compared to the wind speed for all the liquids used in the study, as well as the evaporation rates of all test liquids versus wind speed. The lines shown are those calculated by linear regression. This clearly shows that water evaporation rate increased, as expected, with increasing wind velocity. The oils, ASMB (Alberta Sweet Mixed Blend) and gasoline, do not show rises with increasing wind speed.

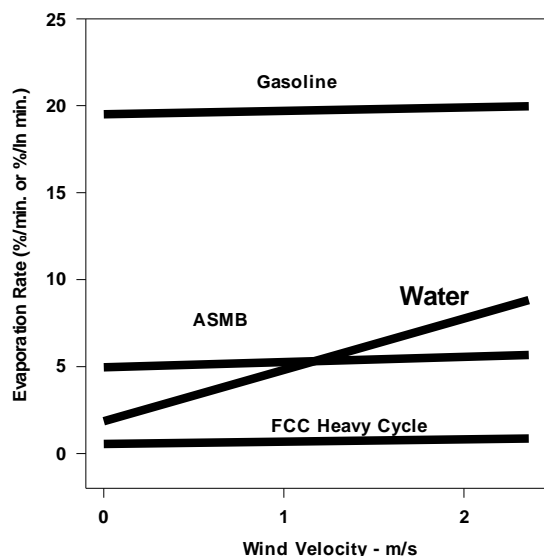


FIG. 4 CORRELATION OF EVAPORATION RATES AND WIND VELOCITY. THE LINES ARE DRAWN THROUGH THE DATA POINTS FROM EXPERIMENTAL VALUES. THIS CLEARLY SHOWS NO CORRELATION OF OIL EVAPORATION RATES WITH WIND VELOCITY AND THE STRONG AND EXPECTED HIGH CORRELATION OF WATER WITH WIND VELOCITY. THE WATER EVAPORATION LINE IS MOVED TO FIT ON THE VERTICAL SCALE, BUT OTHERWISE IS UNALTERED.

These experimental data show that oil is not air boundary-layer regulated. It should be noted that the air movement effect at the lowest level is a stirring effect which increases the diffusion of the components in the oil and thus the evaporation.

### Saturation Concentration

An important concept of evaporation regulation is that of saturation concentration, the maximum concentration of a substance is soluble in air. The saturation concentrations of water and several oil components are listed in Table 1 showing that saturation concentration of water is less than that of common oil components (Fingas, 2011). The saturation concentration of water is in fact, about two orders of

magnitude less than the saturation concentration of volatile oil components such as pentane. This further explains why even light oil components have little boundary layer limitation.

### ***Development of Generic Equations Using Distillation Data***

The evaporation equations for oils show unique differences for oils under the same conditions, implying that unique equations may be needed for each oil and this fact is a significant disadvantage to practical end use. A method to accurately predict evaporation by means of other readily-available data is necessary (Fingas 1999). Findings show that distillation data can be used to predict evaporation. Distillation data are very common and often the only data used to characterize oils. This is because the data are crucial to operating refineries. Crude oils are sometimes priced on the basis of their distillation data.

<b>Table 1 Saturation Concentration of Water and Hydrocarbons</b>		
<b>Substance</b>	<b>Saturation Concentration *</b>	
	in g/m <sup>3</sup> at 25°C	
<b>water</b>	<b>20</b>	
n-pentane	1689	
hexane	564	
cyclohexane	357	
benzene	319	
n-heptane	196	
methylcyclohexane	192	
toluene	110	
ethylbenzene	40	
p-xylene	38	
m-xylene	35	
o-xylene	29	
*Values taken from Ullmann's Encyclopedia		

Oils and diesel-like fuels evaporate as two distinct types, those that evaporate as a logarithm of time and those that evaporate as a square root of time.<sup>1</sup> Most oils typically evaporated as a logarithm (natural) with time. Diesel fuel and similar oils, such as jet fuel, kerosene and the like, evaporate as a square root of time. The reasons for this are simply that diesel fuel and such like have a narrower range of compounds which evaporating at similar rates, yield rates which together sum as a square root.

The empirically measured parameters at 15°C were correlated with both the slopes and the intercepts of the temperature equations. Full details of this correlation are given in the literature (Fingas 2011). For most oils and petroleum products, the variation with temperature resulting equation is:

$$\text{Percentage evaporated} = [B + 0.045(T-15)]\ln(t) \quad (33)$$

where B is the equation parameter at 15°C, T is

temperature in degrees Celsius and t is the time in minutes.

Distillation data were correlated to the evaporation rates determined by experimentation. The optimal point was found to be 180°C by using peak functions. The percent mass distilled at 180 degrees was used to calculate the relationship between the distillation values and the equation parameters. The equations used were derived from correlations of the data. The data from those oils that were better fitted with square root equations - diesel, Bunker C light and FCC Heavy Cycle-were calculated separately. The equations derived from the regressions are as follows:

For most oils that follow a logarithmic equation:

$$\text{Percentage evaporated} = 0.165(\%D) \ln(t) \quad (34)$$

For oils that follow a square root equation such as diesel fuel:

$$\text{Percentage evaporated} = 0.0254(\%D)\sqrt{t} \quad (35)$$

where %D is the percentage (by weight) distilled at 180°C. These equations can be combined with the equations generated in previous work to account for the temperature variations (Fingas 2011):

For oils (most oils and petroleum products) that follow a logarithmic equation:

$$\text{Percentage evaporated} = [.165(\%D) + .045(T-15)]\ln(t) \quad (36)$$

For oils like diesel fuel that follow a square root equation:

$$\text{Percentage evaporated} = [.0254(\%D) + .01(T-15)]\sqrt{t} \quad (37)$$

where %D is the percentage (by weight) distilled at 180°C.

A large number of experiments were performed on oils to directly measure their evaporation curves. Examples of empirical equations obtained are given in Table 2.

### **Complexities to the Diffusion-Regulated Model**

#### ***Oil Thickness***

Studies show that under diffusion regulation very thick slicks (much more than about 2 mm) evaporate slower than other slicks (Fingas 2011). This is due to the increased path length that volatile components must diffuse in a thicker slick. This can certainly be



confused with air-boundary-layer regulation. Experiments by the present author studied the effect of thickness on the evaporation of a light crude oil, Alberta Sweet Mixed Blend (ASMB) crude oil. The equations noted in Table 2 were all measured at a slick thickness of 1.5 mm which is typical of actual at sea values (Fingas 2011). The best curve fit is a square root function from which a correction can be given for thickness.

Corrected equation factor = equation factor +1 - 0.78  $\sqrt{t}$  (38)

Where the corrected equation factor is the factor corrected for the appropriate slick thickness, the logarithmic equation factor is that noted in Table 2, and  $t$  is the slick thickness in mm. This equation is true for thickness values above 1.5 mm at which the original equations were measured.

### *The Bottle Effect*

Another confusing phenomenon to understanding evaporation is the bottle effect. If all the evaporating oil mass is not exposed, such as in a bottle, more oil vapors than those can readily diffuse through the air layer at the bottle mouth may yield a partial or temporary air-boundary-layer regulation effect which may end when the evaporation rate of the oil mass is lower than the rate at which the vapors can readily diffuse through the opening. Such effects could occur in reality in situations such as oil under ice, partially exposed to air or when a thick skin forms over parts of the oil, blocking evaporation.

### *Jumps from the 0-wind Values*

Experimentation shows that studies of oil evaporation at no turbulence or air flow indicate a slight decrease in evaporation rate from those experiments carried out with slight air movement such as found in an ordinary room.<sup>22</sup> This is due to the slight stirring of the oil mass which increases the diffusion rate somewhat. Tests of this phenomenon indicate that further increases in evaporation rate do not occur with increased air movement or turbulence, thus confirming that this is a phenomenon only at 0-wind or turbulence conditions.

### *Use and Comparison of Evaporation Equations in Spill Models*

Evaporation equations are the prime physical change equations used in spill models. A review of the use of evaporation algorithms in oil spill models is given in Fingas, 2011. This is because evaporation is often the

most significant change that occurs in an oil's composition. Many models in the decade after 1984 use the Stiver and Mackay (1984) approach. Currently, more models employ equations such as found in Table 2.

**Table 2 Sample of Empirical Equations of Oil Evaporation**

Oil Type	Equation
Alaska North Slope	%Ev = (2.86 + .045T)ln(t)
Alberta Sweet Mixed Blend	%Ev = (3.24 + .054T)ln(t)
Arabian Medium	%Ev = (1.89 + .045T)ln(t)
Arabian Heavy	%Ev = (2.71 + .045T)ln(t)
Arabian Light	%Ev = (3.41 + .045T)ln(t)
Barrow Island, Australia	%Ev = (4.67 + .045T)ln(t)
Boscan, Venezuela	%Ev = (-0.15 + .013T)/t
Brent, United Kingdom	%Ev = (3.39 + .048T)ln(t)
Bunker C - Light (IFO~250)	%Ev = (.0035 + .0026T)/t
Bunker C - long term	%Ev = (-.21 + .045T)ln(t)
Bunker C (short term)	%Ev = (.35 + .013T)/t
California API 11	%Ev = (-0.13 + .013T)/t
Cano Limon, Colombia	%Ev = (1.71 + .045T)ln(t)
Chavvyo, Russia	%Ev = (3.52 + .045T)ln(t)
Cold Lake Bitumen, AB Canada	%Ev = (-0.16 + .013T)/t
Delta West Block 97, USA	%Ev = (6.57 + .045T)ln(t)
Diesel - long term	%Ev = (5.8 + .045T)ln(t)
Diesel Fuel short term	%Ev = (0.39 + .013T)/t
Ekofisk, Norway	%Ev = (4.92 + .045T)ln(t)
Federated, AB, Canada	%Ev = (3.47 + .045T)ln(t)
Fuel Oil #5	%Ev = (-0.14 + .013T)/t
Gasoline	%Ev = (13.2 + .21T)ln(t)
Gulfaks, Norway	%Ev = (2.29 + .034T)ln(t)
Hout, Kuwait	%Ev = (2.29 + .045T)ln(t)
IFO-180	%Ev = (-0.12 + .013T)/t
Isthmus, Mexico	%Ev = (2.48 + .045T)ln(t)
Jet A1	%Ev = (.59 + .013T)/t
Komineft, Russian	%Ev = (2.73 + .045T)ln(t)
Lago, Angola	%Ev = (1.13 + .045T)ln(t)
Lago Treco, Venezuela	%Ev = (1.12 + .045T)ln(t)
Maya, Mexico	%Ev = (1.38 + .045T)ln(t)
Nugini, New Guinea	%Ev = (1.64 + .045T)ln(t)
Sahara Blend, Algeria	%Ev = (0.001 + .013T)/t
Sakalin, Russia	%Ev = (4.16 + .045T)ln(t)
Scotia Light	%Ev = (6.87 + .045T)ln(t)
South Louisiana	%Ev = (2.39 + .045T)ln(t)
Statfjord, Norway	%Ev = (2.67 + .06T)ln(t)
Taching, China	%Ev = (-0.11 + .013T)/t
Troll, Norway	%Ev = (2.26 + .045T)ln(t)
Udang, Indonesia	%Ev = (-0.14 + .013T)/t
West Texas Intermediate	%Ev = (2.77 + .045T)ln(t)
West Texas Sour	%Ev = (2.57 + .045T)ln(t)

The comparison of air-boundary-layer models with

the empirical equations leads to some interesting conclusions on their applicability. Figure 5 shows a comparison of the prediction of evaporation of diesel fuel using an air-layer-boundary model and an empirical curve. The 0-wind diesel evaporation calculated using an air-layer-boundary model comes closest to the empirical curve, however, prediction is of the wrong curvature. The prediction of diesel evaporation using the wind levels shown, results in prediction errors as great as 100 percent over about 200 hours. Figure 6 shows a comparison of the evaporation of Bunker C using two air-layer-boundary models and an empirical curve. The 0-wind evaporation air-boundary-layer prediction comes closest to the empirical curve. As most comparisons shown, the evaporation rate up to about 8 hours is similar to the empirical curve. The prediction of Bunker C evaporation using the wind levels shown results in prediction errors as great as 400 percent over about 200 hours (direct differential in percentage differences). These high values of Bunker C evaporation as predicted by air-boundary-layer models with wind conditions are completely impossible, as shown by extensive experimentation and field measurements.

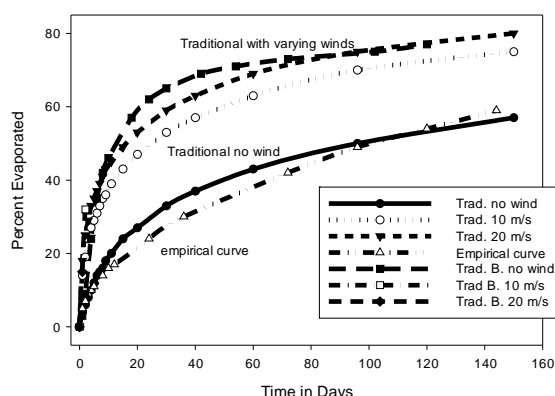


FIGURE 5 A COMPARISON OF THE EVAPORATION OF DIESEL FUEL USING AN AIR-LAYER-BOUNDARY MODEL (SUCH AS FROM EQUATION (30)) AND AN EMPIRICAL CURVE SUCH AS FROM TABLE 2.

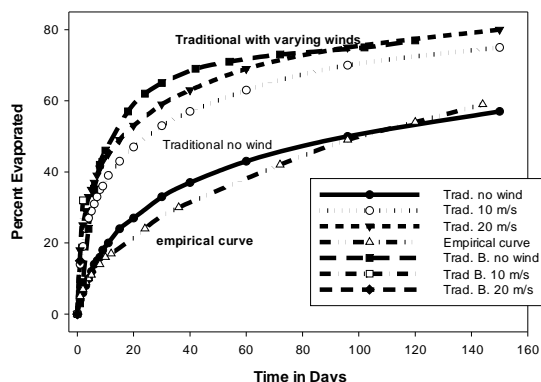


FIG 6 A COMPARISON OF THE EVAPORATION OF BUNKER C USING TWO AIR-LAYER-BOUNDARY MODELS (SUCH AS

FROM EQUATION 30) AND AN EMPIRICAL CURVE (FROM TABLE 2).

The 0-wind diesel evaporation calculated using an air-layer-boundary model comes closest to the empirical curve, however, is of the wrong curvature. The prediction of diesel evaporation using the wind levels shown shows errors as great as 100 percent over about 200 hours.

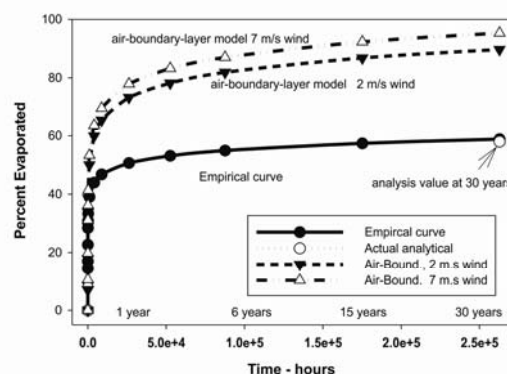


FIG 7 A COMPARISON OF THE EVAPORATION OF PEMBINA CRUDE USING AN AIR-LAYER-BOUNDARY MODEL (EQUATION 30), AN ACTUAL ANALYSIS AFTER 30 YEARS AND AN EMPIRICAL CURVE. THE EVAPORATION RATE UP TO ABOUT 100 HOURS IS SIMILAR TO THE EMPIRICAL CURVE. THE PREDICTION OF LONG-TERM EVAPORATION USING EVEN SMALL WIND LEVELS SHOWN RESULTS IN PREDICTION ERRORS AS GREAT AS 60 PERCENT OVER ABOUT 10 YEARS. THESE HIGH VALUES OF EVAPORATION AS PREDICTED BY AIR-BOUNDARY-LAYER MODELS WITH WIND CONDITIONS ARE NOT REALISTIC.

The 0-wind evaporation prediction comes closest to the empirical curve. The prediction of Bunker C evaporation using the wind levels shown results in prediction errors as great as 400 percent over about 200 hours. These high values of Bunker C evaporation as predicted by air-boundary-layer models with wind conditions are completely impossible. As most comparisons shown, the evaporation rate calculated by most means up to about 10 hours is similar to the empirical curve.

Thus there are three major errors resulting from the use of air-boundary-layer models, and the first and most important is that they cannot accurately deal with long term evaporation; then, the wind factor results in unrealistic values and finally, they have not been adjusted for the different curvature for diesel-like evaporation. Some modelers have adjusted their models using air-boundary-layer models to avoid very high values at long evaporation times by setting a maximum evaporation value, which works after a point in time, but does so artificially. Most models of any type will require that one sets a maximum rate to avoid over prediction or values over 100%, for

example. This can be best illustrated using a long term example. A spill in northern Alberta of Pembina oil was sampled 30 years after its spill. Analysis shows that this was weathered to the extent of 58% (Wang et al. 2004). Figure 7 shows the comparison of the actual value, the empirical projection and the air-boundary-layer predicted value, indicating that the air-boundary-predicted value overshoots the estimate by over 60%, despite the use of only two low wind values of 2 and 7 m/s. Use of higher wind values increases the evaporation to well over 100%.

## Conclusions

A review of oil evaporation shows that oil evaporation is not air-boundary-layer regulated. The results of several experimental series have shown the lack of air boundary-layer regulation. The fact that oil evaporation is not strictly boundary-layer regulated implies that a simplistic evaporation equation will suffice to describe the process. The following factors do not require consideration: wind velocity, turbulence level, area, and scale size. The factors significant to evaporation include time and temperature.

A comparison of the various models used for oil spill evaporation shows that air-boundary-layer models result in erroneous predictions. There are three issues including that air-boundary-layer models cannot accurately deal with long term evaporation; second, the wind factor results in unrealistic values and finally, they have not been adjusted for the different curvature for diesel-like evaporation. There has been some effort made on the part of modellers to adjust air-boundary-layer models to be more realistic for longer-term evaporation but these may be artificial and result in other errors such as under-estimation for long-term prediction.

A diffusion-regulated model has been presented along with many empirically-developed equations for many oils. The equations are found to be of the form shown in equation (34)

It is also noted that in terms of diesel fuel and similar oils the curve is different and follows a square root curve as predicted by equation (35).

The most accurate predictions are carried out using the empirical equations as noted in Table 2. If these are not available, the parameters can be estimated using distillation data as shown by equations (36) and (37).

Marine environments are complex, with many

difference from controlled experiments. It is therefore important to have models that correspond closely to the actual physics to begin to more accurately model phenomena such as evaporation.

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